

Dendronized Polyamides Supports for Mo Catalysts

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ABSTRACT: Dendronized polyamides of generations 1 and 2 were grafted with ethylenediamine (en) ligands at their peripheries by the condensation of chloromethyl groups and en molecules. The obtained dendronized complexes were further equipped with MoO₂acac₂ to form the catalysts PGn-en-Mo. The results of FT-IR and thiocyanate photometric analysis confirmed the successful immobilization of Mo catalysts on dendronized polyamides. The catalytic properties of PGn-en-Mo were first studied in the epoxidation of cyclohexene with tert-butyl hydroperoxide and exhibited high catalytic activity and selectivity. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: dendronized polyamide; ethylenediamine ligand; molybdenum catalyst; cyclohexene epoxidation

Received 25 March 2012; accepted 12 June 2012; published online

DOI: 10.1002/app.38214

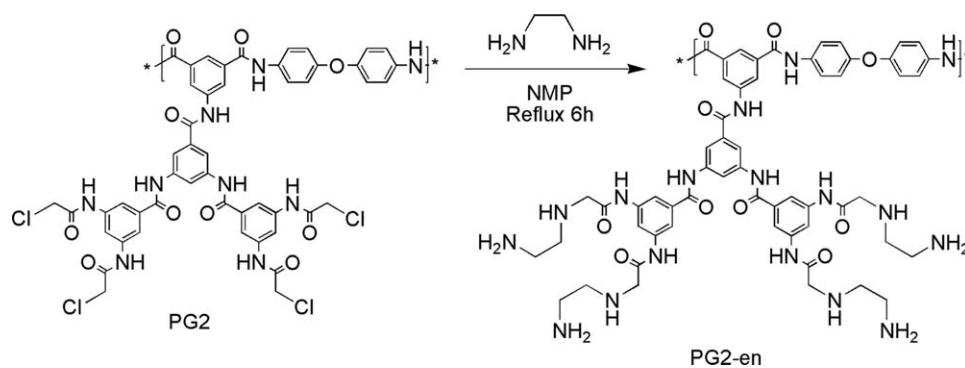
INTRODUCTION

Dendronized polymer, merging both the dendrimer and polymer concepts, has been recently developed.^{1–9} In other words, dendronized polymer is a kind of comb polymer with dendritic side chains pending at every repeating unit along the polymer backbone. With the generation of the dendrons increasing, the structure of these polymers would change from random coil into cylinder, which is due to the steric repulsion between the dendrons of dendronized polymers. At the same time, the dendrons can serve as excellent solubilizers due to their highly branched structure, which improved the solubility of dendronized polymers in same solvent. These rod-like polymers can thus be used as ideal scaffolds for the immobilization of homogeneous catalysts, providing easy separation and recycling of the catalyst via solvent precipitation and filtration, and fine-tuning the catalytic properties of the polymers through the adjustment of the size, structure, and solubility of the pendant dendrons. They may combine the advantages of homogeneous catalysts and heterogeneous catalysts for providing high activity and selectivity under mild conditions.

Dendronized polymers have been investigated as catalyst supports for several kinds of catalysts. van Koten and coworkers¹⁰ equipped the amine functionalized G1–G3 dendronized polymers^{11–14} with NCN-palladium and -platinum pincer complexes.¹⁵ The palladium compounds catalyze the aldol condensation of benzaldehyde with methyl isocyanoacetate, and were found less active than a low molecular weight catalyst, but showed generation-independent. Sasai and coworkers¹⁶ used

polymer-supported bisBINOL ligands to immobilize Al-Li-bis-(binaphthoxide) and μ -oxodititanium catalysts. Both immobilized catalysts promoted the target reactions with high enantioselectivities. Fan and coworkers^{17,18} developed the first optically active dendronized polymeric BINAP ligand as a new type of macromolecular chiral catalyst for asymmetric hydrogenation of simple aryl ketones and 2-arylacrylic acids. Similar to Ru(BINAP) and Ru(BINAP)-cored dendrimers, these dendronized poly(Ru-BINAP) catalysts exhibited high catalytic activity and enantioselectivity. Portnoy and coworkers established effective routes for the construction of poly(aryl benzyl ether),¹⁹ poly(aryl benzyl thioether), and poly(aryl benzyl amine)²⁰ dendrons on polystyrene, and further functionalized with phosphine ligands on the periphery, which complexed with Pd(dba)₂. The first to third generation supported dendritic catalysts exhibited positive dendritic effects in the Heck²¹ and Suzuki²² reactions of bromobenzene. Kowalewska²³ prepared dendronized polystyrenes by the modification of poly(styrene-*co*-chloromethylstyrene) precursors with LiC(SiMe₂CH=CH₂)₃ and attached platinum to the polymers to get a novel catalyst. The catalyst was tested in hydrosilylation of vinylsilanes, and was found to be an interesting alternative for heterogeneous platinum catalysts and Karstedt's catalyst.

Alkene epoxidation is a kind of very useful reaction in industrial organic synthesis. The resultant epoxides are essential precursors in the synthesis of drugs, agrochemicals, and additives. As dendronized polymers have a large number of anchoring points and with the ability of controlling the environment of the



Scheme 1. Synthetic route to PGn-en (PG2-en examples).

catalytic sites at the periphery, they can influence the activity and selectivity of the supported catalysts. Here, we reported the synthesis of dendronized polyamides with $\text{MoO}_2\text{acac}_2$ catalysts incorporation onto the peripheral dendrons, and investigated their application in the cyclohexene epoxidation. To the best of our knowledge, this is the first example about the dendronized polyamide as supports for Mo catalysts.

EXPERIMENTAL

Materials

3,5-diaminobenzoic acid and 5-aminoisophthalic acid were purchased from ABCR GmbH (Karlsruhe, Germany), chloroacetyl chloride, SOCl_2 , 4,4'-oxy-dianiline(4,4'-ODA), ethylenediamine, *N*-methyl-2-pyrrolidone (NMP), ethanol, acetone, acetylacetone, 1,2-dichloromethane, cyclohexene, and tert-butyl hydroperoxide (TBHP) were purchased from Sinopharm Chemical Reagent (Shanghai, China). MoO_3 and K_2CO_3 were purchased from Tianjin Chemical Reagents Four Al-Qaeda Chemical Plant and Tianjin Damao Chemical Reagent Factory (Tianjin, China), respectively. All the agents were of analytical-grade and used as received without further purification.

Synthesis of the Functionalized Dendronized Polyamides

Dendronized aromatic polyamides of generations 1 (PG1) and 2 (PG2) with chloromethyl groups in the periphery were synthesized according to the reported method.²⁴ They were prepared by a macromonomer route with 3,5-diaminobenzoic acid, 5-aminoisophthalic acid, chloroacetyl chloride, and 4,4'-oxy-dianiline(4,4'-ODA) as main components and SOCl_2 as an activating agent.

PG1, IR (KBr, cm^{-1}): 1679, 1556 (amide C=O), 1606, 1506, 1455 (aromatic), 1219 (oxy-phenylene), 674 (C-Cl).

PG2, IR (KBr, cm^{-1}): 1678, 1555 (amide C=O), 1607, 1503, 1454 (aromatic), 1216 (oxy-phenylene), 679 (C-Cl).

Dendronized Polyamides Grafted with Ethylenediamine Ligands

To a 100 mL three-neck flask equipped with a magnetic stirrer and nitrogen inlet was added 20 mL NMP and PGn (4 mmol Cl). The solution was stirred at room temperature until PGn was dissolved in NMP absolutely. Adding 1.6 mL en (24 mmol) and suitable amounts of K_2CO_3 and refluxed under stirring for

6 h. The reaction mixture was poured into methanol and the precipitate was collected by filtration.

PG1-en, IR (KBr, cm^{-1}): 1650, 1539 (amide C=O), 1594, 1495, 1439 (aromatic), 1210 (oxy-phenylene), 1105 (C-N). Elemental analysis, calculated for $\text{C}_{35}\text{H}_{37}\text{N}_9\text{O}_6$: C 61.86, H 5.45, N 18.56; found: C 60.32, H 5.57, N 17.38.

PG2-en, IR (KBr, cm^{-1}): 1657, 1540 (amide C=O), 1601, 1500, 1444 (aromatic), 1223 (oxy-phenylene), 1110 (C-N). Elemental analysis, calculated for $\text{C}_{57}\text{H}_{65}\text{N}_{17}\text{O}_{10}$: C 59.63, H 5.67, N 20.75; found: C 57.18, H 5.92, N 19.03.

Preparation of Polyamide-Supported Molybdenum Catalyst

PG1-en and PG2-en were each loaded with Mo catalyst by reaction with an excess of $\text{MoO}_2\text{acac}_2$ (relative to polyamide-bound ligands). To a 50 mL round bottom flask equipped with a magnetic bar was added 10 mL NMP, PGn-en (2 mmol en), and $\text{MoO}_2\text{acac}_2$ (4 mmol) and refluxed under stirring for 12 h. The reaction mixture was pour into acetone to form precipitate and the sediment was collected by filtration. The excess $\text{MoO}_2\text{acac}_2$ was removed by exhaustive extraction with acetone in a Soxhlet.

PG1-en-Mo, IR (KBr, cm^{-1}): 1655, 1522 (amide C=O), 1601, 1496, 1443 (aromatic), 1218 (oxy-phenylene), 1111 (C-N), 954, 907(O=Mo=O).

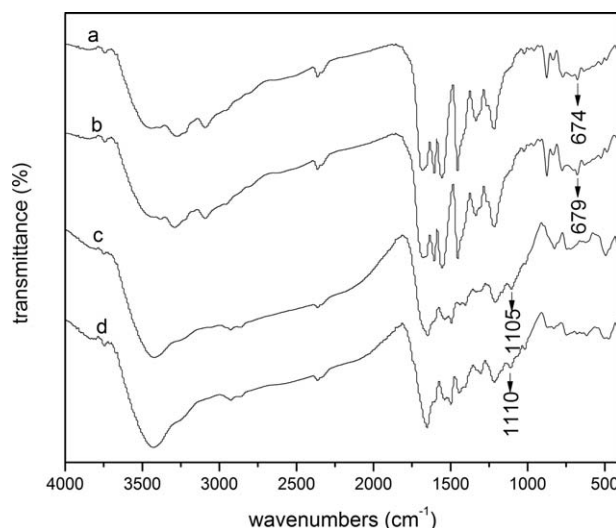


Figure 1. FTIR spectra of (a) PG1, (b) PG2, (c) PG1-en, and (d) PG2-en.

Table I. Elemental Analytical Data for PGn and PGn-en

Polymers	C (wt %) ^a	H (wt %) ^a	N (wt %) ^a	Cl (wt %) ^a
PG1	56.65 (58.86)	3.71 (3.64)	10.44 (11.08)	10.44 (11.23)
PG2	53.06 (55.84)	3.84 (3.51)	11.01 (12.00)	12.32 (13.59)
PG1-en	58.07	5.68	16.99	<0.5
PG2-en	57.18	5.92	19.03	<0.5

^aBracketed values are theoretical assuming full conversion of both monomers.

PG2-en-Mo, IR (KBr, cm^{-1}): 1657, 1525 (amide C=O), 1602, 1502, 1446 (aromatic), 1226 (oxy-phenylene), 1111 (C–N), 946, 913($\text{O}=\text{Mo}=\text{O}$).

Cyclohexene Epoxidation

To a 50 mL round bottom flask equipped with a magnetic bar was added 4 mL 1,2-dichloroethane, 1 mmol cyclohexene, 3 mmol TBHP, and polyamide-supported molybdenum catalysts (0.02 mmol Mo) and refluxed under stirring for 2–6 h. The conversion of reactants and the content of products were analyzed by gas chromatography (GC).

Reusability of the Catalysts

The reusability of the polyamide-supported molybdenum catalysts was studied in repeated epoxidation reaction of cyclohexene. The reactions were carried out as described above. At the end of each reaction, the mixture was filtered and reused without any treatment.

Measurement

Infrared (IR) spectra were recorded with a WQF-410 Fourier transform infrared spectrometer (FTIR; Nicolet, America). Elemental analysis was performed on a Vario EL cube (Elementar, Germany). Thiocyanate photometric method was performed on a UV-2102C ultraviolet visible spectrophotometer (UNICO, China). GC was recorded on a GC-2010 gas chromatograph (Shimadzu, Japan).

RESULTS AND DISCUSSION

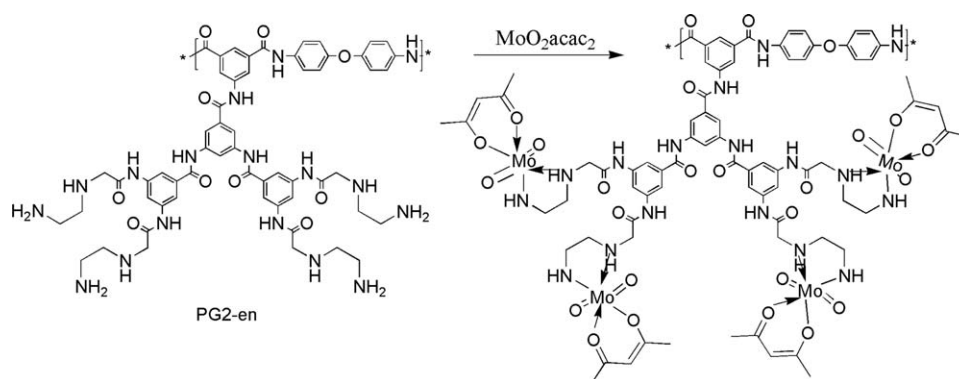
Preparation of Dendronized Polyamides Grafted with Ethylenediamine Ligands

Functionalized dendronized polymers can be modified for advanced application as the groups in the periphery can react with active small molecules and converted to other functional

groups. Ethylenediamine (en) molecules contain active hydrogen atoms in amino groups which can be replaced easily, so en molecules can access to polymer to generate ligands. Dendronized polyamides of generations 1 (PG1) and 2 (PG2) were grafted with en ligands (Scheme 1 illustrates the PG2 routes) by the condensation of the peripheral chloromethyl groups with en ligands in N-methyl-2-pyrrolidone (NMP) under reflux condition for 6 h. The principal evidence for grafting of functional groups onto polymers is the appearance or loss of IR peaks that correspond to the introduction or transformation of distinct functional groups in each stage. In the FTIR spectrum of obtained PGn-en, new peaks appeared at 1105 cm^{-1} for PG1-en and 1110 cm^{-1} for PG2-en that contributed to C–N stretching vibration of aliphatic amine. Further evidence noted by losing of peaks at 674 cm^{-1} for PG1-en and 679 cm^{-1} for PG2-en that were the characteristic of chloromethyl groups (Figure 1). These architectures were also analyzed by elemental analysis. Elemental analysis (Table I) showed that the chlorine contents of PGn-en were less than 0.5%. These characterizations indicated that chlorine was substituted by en ligands.

Preparation of Polyamides-Supported Mo Complex

Ethylenediamine molecules contain two nitrogen atoms with strong coordination ability. After complexed with active center metal, they can form five-membered chelating ring with small tension and stable molecular structure. Reaction of PGn-en with $\text{MoO}_2\text{acac}_2$ in NMP under reflux condition for 12 h resulted in immobilization of $\text{MoO}_2\text{acac}_2$ on dendronized polyamides as shown in Scheme 2. The success of immobilization was confirmed by FTIR spectra as PGn-en-Mo showed the characteristic symmetric and nonsymmetric $\text{O}=\text{Mo}=\text{O}$ stretching bands at 954 cm^{-1} and 907 cm^{-1} for PG1-en-Mo, with 946 cm^{-1} and 913 cm^{-1} for the PG2-en-Mo (Figure 2). The amount of



Scheme 2. Preparation of molybdenum catalyst on PGn-en supports (PG2-en examples).

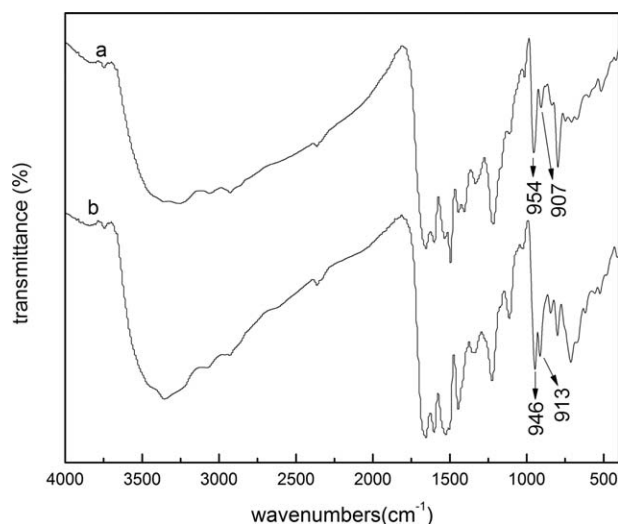


Figure 2. FTIR spectra of (a) PG1-en-Mo and (b) PG2-en-Mo.

molybdenum incorporated into the PGn-en was also determined by thiocyanate photometric method. As can be seen from Table II, PG2-en-Mo had larger Mo/Ligand ratio than PG1-en-Mo, and the Mo/Ligand ratio was greater than 1 for the Mo complexes can be incorporated into intensive amide groups of PG2-en.

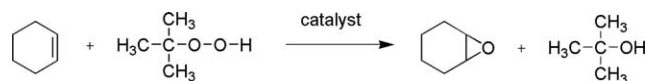
The Study of Catalytic Activity

The catalytic properties of catalysts are vital for the development of catalysts and also become important points for the studies. The catalytic activity of PG1-en-Mo and PG2-en-Mo was initially investigated in the epoxidation of cyclohexene in the presence of TBHP (Scheme 3) in 1,2-dichloroethane. The influence of time to the conversion and selectivity were studied for the reactions. As can be seen from Figures 3 and 4, the optimal reaction time was 4 h because the reactions had greatest conversion and selectivity at that point. When the reactions were kept for 4 h, PG2-en-Mo had the conversion and selectivity value of 89% and 95% separately, and PG1-en-Mo had a little smaller value of 85% both for the conversion and selectivity. Sherrington et al.²⁵ immobilized MoO₂acac₂ on a polystyrene support carrying a hydroxypropylated aminomethylpyridine ligand to obtain a polymer-supported catalyst (PsMo), and studied the catalytic activity of MoO₂acac₂ and PsMo for the epoxidation of cyclohexene by TBHP. The research results of the target reactions that with 1,2-dichloroethane as solvent and under 83°C for 4 h were showed in Table III. Compared to

Table II. Ligand and Mo Loading for PGn-en-Mo

PGn-en-Mo	Mo loading ^a (mmol·g ⁻¹)	Ligand loading ^b (mmol·g ⁻¹)	Mo/Ligand ratio
PG1-en-Mo	1.63	1.76	0.93
PG2-en-Mo	2.07	1.95	1.06

^aFrom thiocyanate photometric method analysis of PGn-en-Mo, ^bFrom elemental analysis of PGn-en based on that all chloromethyl were substituted by en.



Scheme 3. Epoxidation of cyclohexene by dendronized catalysts.

MoO₂acac₂ and PsMo which had the yield of only 55% and 50% separately, PGn-en-Mo exhibited better catalytic activity as they had the yield of 72% and 84% for PG1-en-Mo and PG2-en-Mo, respectively (Table III). Moreover, unlike PsMo which need to be activated with excess TBHP for 18 h at room temperature before became active catalysts, PGn-en-Mo can be used directly without any pretreatment, which will be convenient and economic for the industrial application of PGn-en-Mo.

The reusability of a supported catalyst can be one of the most important benefits as transition metal complexes are often expensive to purchase or prepare. The reusability of supported catalysts have been investigated. PGn-en-Mo were used in epoxidation of cyclohexene in the presence of TBHP for 4 h. Upon

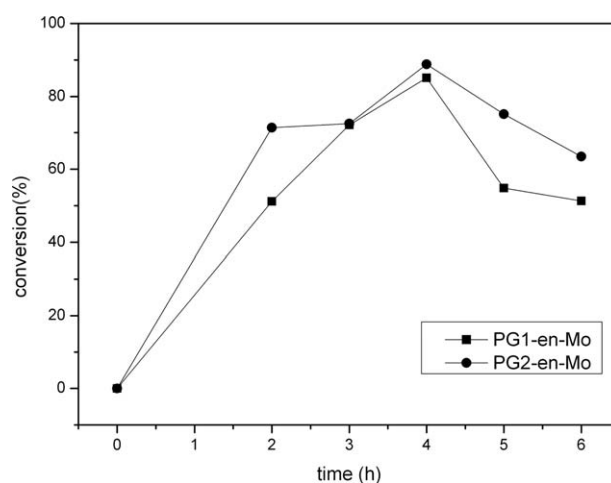


Figure 3. Conversion of epoxidation of cyclohexene with TBHP catalyzed by PGn-en-Mo.

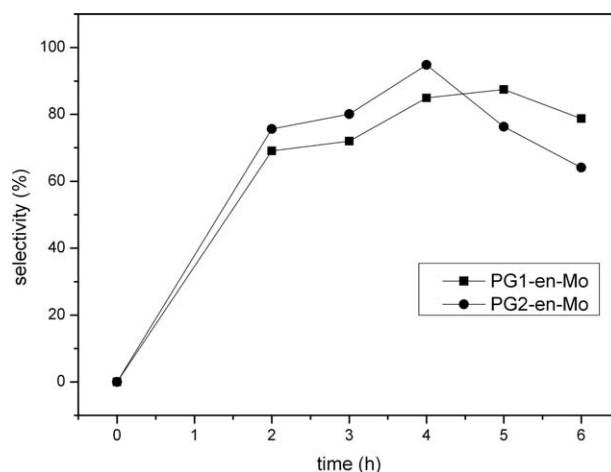


Figure 4. Selectivity of epoxidation of cyclohexene with TBHP catalyzed by PGn-en-Mo.

Table III. Yield of Epoxidation^a of Cyclohexene with TBHP Catalyzed by Different Catalysts

Catalysts	Mo (mmol)	Cyclohexene (mmol)	TBHP (mmol)	Total volume (mL)	Yield (%)
PG1-en-Mo	0.02	1	3	4.5	72
PG2-en-Mo	0.02	1	3	4.5	84
MoO ₂ acac ₂ ²⁵	0.06	5	5	10.5	55
PsMo ²⁵	0.06	5	5	10.5	50

^aThe reactions were kept under reflux condition for 4 h with 1,2-dichloroethane as solvent.

Table IV. Reusability of PGn-en-Mo in Epoxidation of Cyclohexene with TBHP Under Reflux Condition^a

Catalysts	Run	1	2	3
PG1-en-Mo	Yield (%) ^b	72	62	50
PG2-en-Mo	Yield (%) ^b	84	75	68

^aReaction conditions: cyclohexene (1 mmol), TBHP (3 mmol), catalyst (0.02 mmol Mo), 1,2-dichloroethane (4 mL), time (4 h), ^bGC yield based on the starting cyclohexene.

completion of the reaction, the catalysts were filtered and reused in the next reaction without any treatment. The obtained results were showed in Table IV and which indicated that the PGn-en-Mo were reusable as PG1-en-Mo and PG2-en-Mo still had the yield of 50% and 68%, respectively, after three cycles. It is clear that PG2-en-Mo had relatively better activity and cycling stability than PG1-en-Mo. This can be contributed to the fact that PG2-en-Mo had higher dendrons generation with larger surface area and much more intramolecular cavities, and the substrate can contact with catalytic sites more easily and efficiently to produce greater yield.

CONCLUSIONS

In conclusion, we have described a brief preparation of dendronized polyamides-supported en ligands to immobilize Mo catalysts and the obtained catalysts promoted the target reaction with high activity and selectivity. This is the first example of using polyamides containing en ligands to support MoO₂acac₂ catalysts. Further applications toward the immobilization of other catalysts are in progress.

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